L Number	Hits	Search Text	DB	Time stamp
1	0	film-forming-binder and phosphonic near4 oligomer	USPAT; EPO; JPO; DERWENT; IBM_TDB	2003/07/21 09:40
2	0	(film-forming-binder and phosphonic near4 oligomer) and 148/$.ccls.	USPAT; EPO; JPO; DERWENT; IBM_TDB	2003/07/21 09:41
3	0	film adj2 forming adj2 binder and phosphonic near4 oligomer	USPAT; EPO; JPO; DERWENT; IBM_TDB	2003/07/21 09:40
4	116	film adj2 forming adj2 binder and phosphonic	USPAT; EPO; JPO; DERWENT; IBM_TDB	2003/07/21 10:17
5	2	(film adj2 forming adj2 binder and phosphonic) and 148/$.ccls.	USPAT; EPO; JPO; DERWENT; IBM_TDB	2003/07/21 09:45
6	197	(148/259).CCLS.	USPAT; EPO; JPO; DERWENT; IBM_TDB	2003/07/21 09:47
7	167	(148/250).CCLS.	USPAT; EPO; JPO; DERWENT; IBM_TDB	2003/07/21 09:47
8	444	(106/14.12).CCLS.	USPAT; EPO; JPO; DERWENT; IBM_TDB	2003/07/21 09:47
9	332	(252/389.2).CCLS.	USPAT; EPO; JPO; DERWENT; IBM_TDB	2003/07/21 09:48
10	1007	((148/259).CCLS.) ((148/250).CCLS.) ((106/14.12).CCLS.) ((252/389.2).CCLS.)	USPAT; EPO; JPO; DERWENT; IBM_TDB	2003/07/21 10:12
12	6	(film adj2 forming adj2 binder and phosphonic) and wetting adj agent	USPAT; EPO; JPO; DERWENT; IBM_TDB	2003/07/21 10:15
11	4	(((148/259).CCLS.) ((148/250).CCLS.) ((106/14.12).CCLS.) ((252/389.2).CCLS.)) and (film adj2 forming adj2 binder and phosphonic)	USPAT; EPO; JPO; DERWENT; IBM_TDB	2003/07/21 10:12
13	39	film adj2 forming adj2 binder and phosphonic and (clean$4 or degreas$4)	USPAT; EPO; JPO; DERWENT; IBM_TDB	2003/07/21 10:18

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Foreword

Volume 13 of the *Metals Handbook* series was compiled in response to the demand from our membership for a detailed work on the multibillion-dollar problem that confronts nearly every design engineer in every industry: corrosion. It represents the culmination of three years of intensive planning, writing, editing, and production. The hard work has paid off. *Corrosion* is the largest, most comprehensive volume on a single topic ever published by ASM.

We believe that our readers will find this Handbook useful, instructive, and enlightening. These pages cover every aspect of the subject: corrosion theory, forms of corrosion, testing and evaluation, design considerations, protection methods, and corrosion as it affects specific metals and alloys and specific industries. Our goal is to help you solve existing corrosion problems--and to help you prevent problems in the future.

ASM INTERNATIONAL is indebted to Lawrence J. Korb, Co-chairman of the Handbook and the driving force behind the project, and to Co-Chairman David L. Olson. Their task of planning and coordinating this volume has been a yeoman's one, and they have been equal to it. Both Larry and Dave are Fellows of ASM and have served in leadership roles within the Society for many years--Larry as a past Chairman of the Publications Council and the Handbook Committee, and Dave as a past Chairman of the Joining Division Council and as a member of the Handbook Committee since 1982. They epitomize the vast pool of talent and energy made available to the Sociey by its dedicated members, without whom we could not survive. Thanks also go to the ASM Handbook Committee and to the ASM editorial staff for their tireless efforts.

We are especially grateful to the nearly 500 authors and reviewers listed in the next several pages. Their generous commitment of time and expertise, their willingness to share their years of experience and knowledge, to write and rewrite, has made this Handbook a truly outstanding source of information.

- Raymond F. Decker
  President
  ASM INTERNATIONAL
- Edward L. Langer
  Managing Director
  ASM INTERNATIONAL

Preface

The cost of corrosion to U.S. industries and the American public is currently estimated at $170 billion per year. Although corrosion is only nature's method of recycling, or of returning a metal to its lowest energy form, it is an insidious enemy that destroys our cars, our plumbing, our buildings, our bridges, our engines, and our factories. Corrosion can often be predictable, such as the uniform corrosion of steel ship hulls or tanks, or it can be totally unpredictable and catastrophic, such as the hydrogen embrittlement or stress corrosion of critical structural members and pressure vessels in the aerospace and chemical processing industries. While corrosion obeys well-known laws of electrochemistry and thermodynamics, the many variables that influence the behavior of a metal in its environment can result in accelerated corrosion or failure in one case and complete protection in another similar case. We can no longer think of materials and environments as monolithic. It makes no sense to ask whether stainless steel is compatible with sulfuric acid. Rather, the question we must ask is which alloy of stainless steel, with which microstructure, with which design detail, is compatible with which sulfuric acid. What is the acid's temperature, concentration, pH, impurity level, types of trace species, degree of aeration, flow velocity, etc.?

Avoiding detrimental corrosion requires the interdisciplinary approach of the designer, the metallurgist, and the chemist. Sooner or later, nearly everyone in these fields will be faced with major corrosion issues. It is necessary to learn to recognize the forms of corrosion and the parameters that must be controlled to avoid or mitigate corrosion. This Handbook was written with these three engineering disciplines in mind. We have attempted to put together a reference book that is well rounded and complete in its coverage--for we want this to be the first book you select when researching a corrosion problem. Each article is indexed to other appropriate sections of the Handbook, and each provides a road map to the thousands of individual bibliographical references that were used to compile the information.

The Handbook is organized into eight major Sections. The first is a Glossary of metallurgical and corrosion terms used throughout the Volume. Nearly 600 terms are defined, selected from more than 20 sources. Of course, one of the most difficult terms to get corrosion experts to agree upon is a definition for "corrosion" itself, for where does one draw the line? Is not the hydride, which precipitates in a stressed titanium weld, a form of corrosion just as the hydrogen embrittlement of steel? And where does corrosion stop--with a metal, or is the environmental reaction of a ceramic or polymer also a form of corrosion? In this Handbook we have limited our discussion of corrosion to metals, by and large, but have included reactions with external environments which may diffuse inside a metal, leading to its destruction as an "internal environment."

The second Section covers the theory of corrosion from the thermodynamic and kinetic points of view. It covers the principles of electrochemistry, diffusion, and dissolution as they apply to aqueous corrosion and high-temperature corrosion in salts, liquid metals, and gases. The effects of both metallurgical and environmental variables on corrosion in aqueous solutions are discussed in detail.

The third Section describes the various forms of corrosion, how to recognize them, and the driving conditions or parameters that influence each form of corrosion, for it is the control of these parameters which can minimize or eliminate corrosion. For convenience, this Section is divided into articles on general corrosion, localized corrosion, metallurgically influenced corrosion, mechanically assisted degradation, and environmentally induced cracking. More than 20 distinct corrosion mechanisms are discussed.

mIn the fourth Section, methods of corrosion testing and evaluation in the laboratory as well as in-place corrosion monitoring are discussed. For each major form of corrosion (pitting, stress-corrosion cracking, etc.), the existing techniques used in their evaluation are discussed along with the advantages and limitations of each particular test and the quality of the test data generated.

The fifth Section looks at corrosion from the design standpoint. Which materials and design details minimize corrosion? What are the corrosion problems with weldments and how can they be addressed? Finally, how do you place an economic value on your selection of alternate materials or coatings?

The next Section reviews the various methods used for corrosion protection. These include surface conversion coatings, anodizing, ceramic coatings, organic coatings, metallic coatings (both as barrier metals and as sacrificial coatings), thermal spray coatings, CVD/PVD coatings, and other methods of surface modification. It also discusses the principles of and the approaches to anodic and cathodic protection. Finally, the various types and uses of corrosion inhibitors are thoroughly discussed.

The seventh Section covers the corrosion of 27 different metal systems, including all major structural alloy systems and precious metals, and relates the latest information on such topics as powder metals, cemented carbides, amorphous metals, metal matrix composites, hard chromium plating, brazing alloys, and clad metals. In many areas, complete articles have been written where only a few paragraphs were available in existing corrosion texts. For each metal system, the authors discuss the alloys available, the nature of the corrosion resistance film that forms on the metal, and the mechanisms of corrosion, including the metallurgical factors or elements that inhibit or accelerate corrosion. Various forms of corrosion are discussed as well as various environmental effects. The behavior of these metal systems in atmospheres (rural, marine, industrial), in waters (fresh water and seawater), and in alkalies, acids, salts, organic chemicals, and gases is discussed. Methods of corrosion protection most applicable to each metal system are reviewed.

The final Section of the Handbook is where all of this knowledge is put into practice. It vividly illustrates how far we've come in understanding and combating corrosion and how far we have yet to go. The corrosion experiences of experts from 20 major industries are covered in detail--from fossil fuels to nuclear power, from the chemical processing to the marine industries, from prosthetic devices to the space shuttle, from pharmaceuticals to electronics, from petroleum production and refining to heavy construction. The authors describe the corrosion problems they encounter, tell how they solve them, and present illustrated case histories.

We think you will find this Handbook a broad-based approach to understanding corrosion, with sufficient data and examples to solve many problems directly, and references to key literature for further research into highly complex corrosion issues. There is no cookbook for corrosion avoidance! We hope this Volume with its road map of references will lead you to a better understanding of your corrosion problems and assist you in their solutions.

This Handbook would not have been possible without the generous contributions of the nearly 500 leading corrosion experts who donated their expertise as authors and reviewers. They represent many of

the leading industries and educational institutions in this country and abroad. The articles in this Handbook represent tremendous individual efforts. We are also grateful to the Handbook staff at ASM INTERNATIONAL and for the extremely valuable contributions of several technical societies and industrial associations, including the National Association of Corrosion Engineers, the American Society for Testing and Materials, the Electric Power Research Institute, the Pulp and Paper Research Institute of Canada, the Tin Research Institute, the Institute of Paper Chemistry, the American Hot Dip Galvanizers Association, and the Lead Industries Association. In addition, we particularly appreciate the efforts of those who took responsibility for coordinating authors and papers for many articles or entire Sections of this Volume: Dr. Miroslav Marek, Dr. Bruce Craig, Dr.Steven Pohlman, Mr. Donald Sprowls, Mr. James Lackey, Dr. Herbert Townsend, Dr. Thomas Cape, Mr. Kenneth Tator, Dr. Ralph Davison, Dr. Aziz Asphahani, Mr. R. Terrence Webster, Mr. Robert Charlton, Mr. James Hanck, and Mr. Fred Meyer, Jr.

This has truly been a collective venture of the technical community. We thank those who willingly have shared their knowledge with all of us.

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C pyright Information (for Print Volume)

ASM Handbook is a collective effort involving thousands of technical specialists. It brings together in one book a wealth of information from world-wide sources to help scientists, engineers, and technicians solve current and long-range problems.

Comments, criticisms, and suggestions are invited, and should be forwarded to ASM International.

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Cleaning for Surface Conversion

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Contaminants and Some Methods of Removal

Any substance that inhibits or interferes with the application of the conversion coating, the adhesion and reactivity of the conversion coating, and/or the subsequent adhesion of the organic coating is a contaminant that must be removed. Some contaminants are easier to remove than others. Most nonadhering contaminants can be flushed off with the cleaner, but contaminants that are part of the metal surface must first be put into solution by the cleaner. Some contaminants are too difficult for the cleaner alone to remove; therefore, they are mechanically removed with abrasive brushes (see the article "Painting" in *Surface Engineering,* Volume 5 of the *ASM Handbook*). In some cases, an acid pickle may be required to remove such surface contaminants as aluminum and carbon smut, metal fines, surface rust, and scale.

A nonuniform reaction of the conversion coating with the metal surface will cause adhesion failure of the conversion coating and the subsequent organic coatings. Different contaminants prevent reaction of the conversion coating to the metal surface in different ways. Residual organic soil prevents contact of the aqueous conversion coating with the metal surface. Inorganic soil undermines the integrity of the conversion coating. Metal oxides that remain on the surface will be sites of future galvanic action under the subsequent organic coating. This can result in premature failure of the finished product because of underfilm corrosion.

Oils. Several different types of oils may be deposited on the surface of the metal. Stamping oils, rolling oils, machining oils, corrosion protection oils, and combinations of these are some of the types that may be encountered. The quantity of oil and the ease of removal depend on the length of time and the conditions of storage, the original use of the oil, and the type of metal to be protected. Lubricating oils are easier to remove than rust-preventive oils. Lubricating oils usually have emulsifiers to facilitate cleaning, but rust-preventive oils have additives that enhance their water-repellent qualities.

Because oil is insoluble in water, it interferes with the proper deposition of aqueous conversion coatings. To remove oils from the metal surface, several different surfactants (surface-active agents), such as detergents or wetting agents, can be added to the cleaner. The surfactants reduce the surface tension of the water and permit the cleaning solution to contact the metal surface. The concentration of surfactants in a cleaner has significant effect on the time required to penetrate the soil. Inadequate quantities will slow the cleaning process.

Cleaning time is decreased as the concentration of surfactants is increased, until a point is reached at which the addition of more surfactant does not reduce the cleaning time. This point may vary with changes in temperature, soil conditions, and type of metal being cleaned. The optimum surfactant concentration is determined by the percentage that will penetrate the soil in a required time at a minimum cost (Fig. 1).

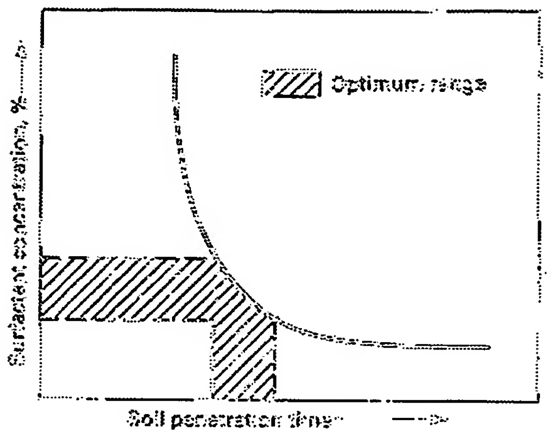

Fig. 1 Relationship between concentration of surfactants in a cleaner and cleaning time

Detergents, in addition to being surfactants, may emulsify the oils. Most of the strong synthetic detergents can be categorized as anionic, cationic, or nonionic. Anionic detergents are surfactants in which the active portion is a negative ion (anion). This type of detergent usually has the best detergency, along with high-foam characteristics. Cationic detergents are surfactants in which the positive ion (cation) is the active portion. These are usually good emulsifiers. Nonionic detergents do not ionize. They are valued for their low-foaming characteristics and are the most commonly used type of detergent.

Carbon is often found on products that are rolled from hot ingots or are continuously cast. One source of carbon is when rolling oil is subjected to the excessive temperature encountered during the reduction process. Carbon residue is very difficult to remove because of its nonreactive nature. Carbon that is left on the metal surface can cause voids or bridges within the conversion coating that appear later as poor adhesion. One method for testing the amount of carbon on the metal surface is the Ford LECO Swab Test (Ford specification ESB-M2PX).

If the amount of carbon on the surface is not too high, it can be removed by mechanical means, such as brushing. The type of brushes used will vary with the type of metal to be cleaned. Generally, if the surface carbon is determined to exceed 6.5 mg/m^2 (0.6 mg/ft^2) as measured by the Ford test, additional acid pickling must be done to clean the surface adequately. For a chemical cleaner to remove carbon, additives that have a greater attraction for carbon than the attractive force between carbon and the metal surface must be incorporated into the cleaner.

Metal Fines and Scale. Certain rolling practices often leave metal dust or small pieces of metal adhering to the metal surface. These are called metal fines. Scale is the oxidized surface of steel, produced during heating for working the steel, that has been rolled into the surface of the metal. These contaminants shield the metal surface from the conversion coating, but when under stress, they may later separate from the metal surface, leaving it unprotected. A cleaner can lower the surface tension to wash off the metal fines, or it can dissolve them. Mechanical means are also used. The method of removal is determined by the quality of metal fines as well as the type of metal being cleaned.

Scale, if it cannot be dissolved, must also be mechanically removed. A preliminary cleaning in an acid-pickling solution is often necessary. More information on pickling ferrous metals is available in the article "Pickling and Descaling" in *Surface Engineering,* Volume 5 of the *ASM Handbook,* formerly 9th

Edition *Metals Handbook.*

Passivation coatings are applied to electroplated zinc, hot-dip zinc, and zinc-aluminum alloy coatings applied on steel substrates. Passivation treatments are applied at the time of production to prevent white rust during transportation and storage. Examples of some types of passivation coatings are straight chromic acid (H_2CrO_4), sodium dichromate-sodium silicate ($Na_2Cr_2O_7$-Na_2SiO_3), and blends of various additives in conjunction with $Na_2Cr_2O_7$ and/or H_2CrO_4). Some types of conversion coatings can be properly applied over some types of passivation coatings, but others cannot. Passivation coatings containing resins or silicate will not permit any conversion coating over the passivation coating. If the conversion coating cannot be applied to the particular passivation coating, the passivation coating must be removed.

Removal of the passivation coating from the metal surface can be extremely difficult, especially if the passivation coating has aged and completely reacted. Cleaner solutions have difficulty in removing reacted passivation coatings. Mechanical means must be relied on; therefore, uniformity of cleaning is very difficult to achieve with passivated substrates.

Metal oxides are the products of corrosion or high-temperature oxidation of the metal surface. Metal oxides are formed through the natural reaction of the metal surface with oxygen, usually in the presence of moisture. They form a loose, spongy matrix that is not conducive to good adhesion of organic coatings on the metal surface. Metal oxides will not react with the conversion coating to form a corrosion-inhibiting barrier. Left on the surface within a conversion coating, they will accelerate further corrosion of the remaining substrate. For these reasons, metal oxides must be removed before the conversion coating is applied.

Selection of the cleaner is based on the metal to be cleaned and the type of equipment available. Metal substrates such as zinc, aluminum, steel, or combinations of these metals vary in solubility in the type of cleaner used. For example, aluminum oxide is usually only slightly soluble in acid cleaners, but it is very soluble in alkaline cleaners. Zinc oxide is soluble in both acid and alkaline cleaners. Iron oxide is soluble in acid cleaners.

The primary constituents of an alkaline cleaner may be sodium hydroxide (NaOH) or potassium hydroxide (KOH). An acid cleaner can be based on an organic phosphate or an acid, such as phosphoric acid (H_3PO_4) or acetic acid. These constituents are usually referred to as the backbone of the cleaner. Care should be taken to ensure that the backbone does not react with nonoxidized metal on the surface. When this is permitted to occur, metal compounds are deposited on the surface that interfere with the formation of the conversion coating and its adhesion. Aluminum hydroxide ($Al(OH)_3$) (aluminum smut), zinc hydroxide ($Zn(OH)_2$), and zinc phosphate ($Zn_3(PO_4)_2$) are examples of these metal compounds. The formation of these metal compounds is prevented by the use of buffers that inhibit the reaction of the cleaner with the metal surface. If this is not effective, additional processing steps, such as smut removal, must be taken.

A buffer consists of an acid or an alkali in the form of a salt, such as borate, phosphate, or silicate. A buffering agent enables the use of a higher concentration of the cleaner. If silicates are used as the buffer, adequate rinsing should be provided because of their poor rinsing qualities. More information on alkaline and acid cleaners is available in the articles "Alkaline Cleaning" and "Acid Cleaning," respectively, in

Surface Engineering, Volume 5 of *ASM Handbook*, formerly 9th Edition *Metals Handbook*.

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